

Atmospheric Nitrogen Deposition in South–East Scotland: Quantification of the Organic Nitrogen Fraction in Wet, Dry and Bulk Deposition

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Abstract

Water soluble organic nitrogen (WSON) compounds are ubiquitous in precipitation and in the planetary boundary layer, and therefore are a potential source of bioavailable reactive nitrogen. This paper examines weekly rain data over a period of 22 months from June 2005 to March 2007 collected in 2 types of rain collector (bulk deposition and “dry+wet” deposition) located in a semi-rural area 15 km southwest of Edinburgh, UK (N 55°51'44", W 3°12'19"). Bulk deposition collectors are denoted in this paper as “standard rain gauges”, and they are the design used in the UK national network for monitoring precipitation composition. “Dry+wet” deposition collectors are flushing rain gauges and they are equipped with a rain detector (conductivity array), a spray nozzle, a 2-way valve and two independent bottles to collect funnel washings (dry deposition) and true wet deposition. On average, for the 27 weekly samples with 3 valid replicates for the 2 types of collectors, dissolved organic nitrogen (DON) represented 23% of the total dissolved nitrogen (TDN) in bulk deposition. Dry deposition of particles and gas on the funnel surface, rather than rain, contributed over half of all N-containing species (inorganic and organic). Some discrepancies were found between bulk rain gauges and flushing rain gauges, for deposition of both TDN and DON, suggesting biological conversion and loss of inorganic N in the flushing samplers.

Keywords

Water soluble organic nitrogen, DON, reactive nitrogen, bulk deposition, wet deposition, dry deposition, rain collector

Introduction

In recent years there has been a growing concern that dissolved organic nitrogen (DON) compounds can contribute significantly to the nutrient budgets of many ecosystems and, therefore, to eutrophication processes (Cornell *et al.*, 2003). Organic nitrogen compounds also influence atmospheric chemistry and air quality (Nakamura *et al.*, 2006) and, in water treatment, DON compounds are an emerging concern as precursors for carcinogenic disinfection byproducts such as haloacetonitriles and N-nitrosodimethylamine (Ambonguilat *et al.*, 2006, Lee and Westerhoff, 2005, Westerhoff and Mash, 2002).

One of the main limitations in DON determination in water samples is that it is not possible to quantify directly (Cape *et al.*, 2001, Jones and Willett, 2006, Vandenbruwane *et al.*, 2007, Zhang *et al.*, 2008). DON concentration is calculated by the subtraction of several independently measured concentrations, which leads to an important analytical uncertainty (Lee and Westerhoff, 2005, Vandenbruwane *et al.*, 2007). For this reason, and other difficulties associated with organic nitrogen species analysis, most of the studies regarding N budgets to date have been conducted only on the inorganic nitrogen species. In Europe, the reactive nitrogen compounds restricted under the Gothenburg Protocol (UN-ECE, 1999) and the EU Directive 2001/81/EC (EU, 2001), both aiming to limit emissions of acidifying and eutrophying pollutants and ozone precursors, only include nitrogen oxides (NO_x) and ammonia (NH₃) and their roles as precursors of inorganic N deposition in precipitation. However, atmospheric DON deposition has been estimated to represent on average 30% of the total dissolved nitrogen (TDN) in precipitation in the UK (Cape *et al.*, 2004) and varying proportions (both higher and lower) elsewhere (Cornell *et al.*, 1995, Cornell and Jickells, 1999, Cornell *et al.*, 2003, Neff *et al.*, 2002).

The atmospheric organic nitrogen fraction is believed to include a large spectrum of natural compounds such as amino acids and urea, and small amounts of synthetic compounds such as atrazine (Ambonguilat *et al.*, 2006), or reaction products from man-made emissions, such as nitrophenols (Luttke *et al.*, 1997), but in spite of the importance of ON in the global N budget, the chemical forms and sources of ON are not yet sufficiently understood.

An important and yet unanswered question is the atmospheric ON origin: natural, anthropogenic or mixed? Due to the important contribution of the ON fraction to the total N budget, this is a key question when assessing the scale of the human perturbation of the N cycle. To date, investigations of individual compounds and isotopic analysis have been unable to provide conclusive results regarding the origin of atmospheric ON (Kelly *et al.*, 2005). In a recent study over the East China Sea and western North Pacific it was suggested that water soluble organic nitrogen (WSON) compounds in marine aerosols were mainly from anthropogenic origin, as they were associated with continental materials of anthropogenic origin, particularly NH₄⁺ in fine particles (Nakamura *et al.*, 2006). On the other hand, another study (Pacheco *et al.*, 2004) claimed that WSON represents up to 90% of the total soluble nitrogen found in tropical continental rain in remote unpolluted sites, suggesting a natural origin.

Another crucial question is whether the main contributor to the ON fraction in terrestrial ecosystems is dry or wet deposition. Wet deposition denotes removal by clouds and falling precipitation, and dry deposition denotes the direct collection of gases and particulates on a

surface. In this context, a number of methods and different designs have been described for rain sampling over the last 30 years (Dämmgen *et al.*, 2005). However, despite several studies showing that dry deposition can contribute significantly to nitrogen in bulk precipitation (Cape and Leith, 2002), in many cases, precipitation composition is derived from measurements of bulk precipitation, i.e. the basic design comprises a funnel connected to a collecting bottle, and therefore does not discriminate between dry deposition to the surface of the funnel and nitrogen species dissolved in the rain. There have been many studies aimed at evaluating the contribution of dry deposition to bulk precipitation collectors (Cape *et al.*, 2009, Lee and Longhurst, 1992) but none so far has explicitly considered the effect on water-soluble organic nitrogen.

In summary, very little is known with regard to organic nitrogen in the atmosphere and in precipitation, and to its source and sink budgets. To date very important questions such as deposition mechanisms remain unanswered: wet vs. dry deposition; natural, anthropogenic or mixed origin; composition and biological availability. The aim of the work presented in this paper is to measure the organic nitrogen fraction dissolved in precipitation, and to discriminate between what is coming from dry and wet deposition.

Experimental

Study site and collection methods

Precipitation was sampled weekly from June 2005 to April 2007 at the Centre for Ecology and Hydrology, in a 'science park' and within 1 km of mixed farming (arable and dairy) 15 km southwest of Edinburgh, UK (N55°51'44", W3°12'19"). Two types of rain collector were used in this study: standard rain collectors and flushing rain collectors. Three rain collectors of each type were mounted 1.5 m above ground, in a 5 m-side square, in the middle of a grass field. The standard rain collectors consisted of a polypropylene funnel diameter 152 mm mounted directly in a polypropylene collecting bottle, and is the design used in the UK national network for monitoring precipitation composition (Cape *et al.*, 2001). The flushing rain collectors (Cape *et al.*, 2009) are equipped with a rain detector (conductivity array), a spray nozzle, an identical polypropylene funnel to the standard collector, a 2-way PTFE motorized valve, and two independent collecting bottles at ground level, connected to the funnels by 1.5m lengths of silicone tubing enclosed in an opaque flexible PVC tube (to exclude light and minimise biological activity). When a rain event is detected, the funnel is rinsed with a fixed volume of 10% methanol in distilled water and the washings are collected in one of the sampling bottles as a measure of dry deposition on the funnel surface since the last precipitation event. One minute after the rinsing, the 2-way valve is switched to allow the subsequent rain, free from any contamination by prior dry deposition, to enter the second rain sample bottle. At the end of a rain event, signalled by the rain detector, the valve is switched again to the 'divert' position to seal the rain sample bottle from the atmosphere.

Sample Preservation

Nitrogen containing compounds in precipitation are especially vulnerable to biological degradation (Cape *et al.*, 2001, Hadi and Cape, 1995). For this reason there is a need for preservation of the sample during the processes of collection, transportation and storage. In this study, a small amount of a biocide solution was added to the collection bottles prior to

sampling. Thymol (2-isopropyl-5-methyl phenol) was the biocide of choice in this study, as it is non-volatile, effective at low concentrations, and presents few toxicity problems for disposal. 100 mg L⁻¹ was previously determined to be the optimum concentration (Cape et al., 2001, Hadi and Cape, 1995). This was the target concentration when sample bottles for rainfall and washings were charged with 25 mg thymol per litre of capacity before use (1 mL and 0.5 mL of 50 g L⁻¹ methanol solution for rain and washings, respectively). The final thymol concentration in each sample was therefore variable, depending on the amount of rain during each particular week. However, the biocidal effect is not diminished greatly even if the sample bottle is filled (Cape et al., 2001). Collected rain samples were stored at 4 °C before analysis. Samples were filtered through a 0.2 µm pore-size inorganic membrane filter (Whatman, Anotop 10 IC) before chemical analysis.

Detection Techniques & Instrumentation

Dissolved organic nitrogen (DON) concentrations in water samples cannot be quantified directly. Analysis involves several steps: determination of the total dissolved nitrogen (TDN) concentration, determination of the dissolved inorganic nitrogen species (DIN) concentration, and finally subtraction of DIN concentrations from the TDN concentrations. TDN includes all nitrogen containing species (organic and inorganic) dissolved in the sample. DIN includes all the nitrates (NO₃⁻), nitrites (NO₂⁻) and ammonium (NH₄⁺) dissolved in the sample.

Total Dissolved Nitrogen (TDN) Determination Methods

TDN determination requires a preparatory digestion step, either chemical or by combustion. The main digestion methods available and in current use for total nitrogen determination in aqueous samples are: Kjeldahl digestion (Doval et al., 1997, Nozawa et al., 2005, Yasuhara and Nokihara, 2001), alkaline persulphate oxidation (Cape et al., 2001, Cornell et al., 2003, Scudlark et al., 1998) and high-temperature catalytic oxidation (Cape et al., 2001, Cornell et al., 2003, Keene et al., 2002).

High-temperature catalytic oxidation (HTCO) was the method of choice in this study. This method aims for the complete combustion of all organic material to CO₂ and nitric oxide (NO), followed by quantitative detection of nitric oxide (NO) by chemiluminescence. The instrument used for this technique was a Nitrogen Specific HPLC Detector, ANTEK 8060-M, operated according to the manual. The analysis was conducted in flow-injection mode, with triplicate analysis of a 20 µL sample in a carrier of deionised water at a flow rate of 250 µL min⁻¹. Typical detection limit for TDN was 1 µM N, based on independent calibration with standard solutions of ammonium sulphate and sodium nitrate. Prior tests had shown that the ANTEK system converts all but the most intransigent organic compounds quantitatively (Cape et al., 2001).

Dissolved Inorganic Nitrogen (DIN) Determination Methods

Ion chromatography was the method of choice for dissolved inorganic nitrogen determination. The equipment used included a Metrohm 766 IC Sample Processor connected in parallel to a Metrohm 733 IC Separation Centre equipped with a Metrosep C1 column for ammonium determination, using 24 mM boric acid / 5 mM tartaric acid / 0.7 mM dipicolinic acid eluent, and to a Metrohm 761 Compact IC equipped with a Metrosep A Supp 5 column, with 3.2 mM carbonate / 1.0 mM bicarbonate as eluant, for nitrate and nitrite determination. Typical detection limits were 0.5 µM for NH₄⁺ and 0.4 µM for NO₃⁻ for a 250 µL injection. The cation

analysis also quantified potassium concentrations in the sample, used to identify potential contamination (see below)

Limit of detection for DON

The limit of detection for the individual analytes (above) was defined as 3 times the SD of the blanks. The variance of DON is defined as the summation of the variance of the 3 independent measured concentrations (TDN, NH_4^+ & NO_3^-). Therefore, the limit of detection of DON would be $1.2 \mu\text{M N}$. However, samples with DON under this limit of detection, and even with small negative values, have been included in the statistical analysis, as to have discarded an otherwise valid sample only on the grounds of low or negative DON concentration would have biased the statistical analysis towards the samples with higher DON concentrations.

Criteria used to establish sample quality

Two criteria were used to identify valid precipitation samples: (i) free from obvious contamination: K^+ concentration must be lower than $20 \mu\text{M}$, as K^+ is a good marker for biological contamination (in this study, normally due to bird droppings). 6% of the samples collected were discarded for this reason. (ii) The sample must have sufficient amount of rainfall: the minimum volume was set at 50 mL. Samples with lower volumes were discarded, as they are more vulnerable to alterations in original composition, mainly due to evaporation or condensation processes. 7.5% of the samples collected were discarded for this reason.

The sampling period comprised 92 weeks, from 17th June 2005 to 28th March 2007. For statistical analyses only those weeks with three valid collector replicates for each type of collector were included, limiting the set of samples to 41 weeks. Weeks with three valid samples but with relative standard deviation (RSD) in the total dissolved nitrogen (TDN) greater than 50%, either in bulk deposition or in (dry + wet) deposition, were regarded as “suspicious” and removed from the statistical analysis, as the important discrepancies observed in those weeks within collectors of the same type (either standard rain gauges or flushing rain gauges) might suggest that an unnoticed problem had occurred in one or more of the collectors during that particular period. Seven of the 41 remaining weeks were discarded for this reason. Two additional weeks were removed from the statistical analysis, as mineral nitrogen fertilizer was being applied to a nearby field on these dates.

Results

Dissolved Organic Nitrogen (DON)

Dissolved organic nitrogen (DON) represents a significant fraction of the N-containing species in all types of rain gauge (bulk, washings and wet deposition) over the whole period of study. Figures 1, 2 and 3 show the time series of the average amount of DON and DIN collected in the bulk, wet deposition and funnel washings (dry deposition) fractions, respectively, as $\mu\text{moles N m}^{-2} \text{wk}^{-1}$.

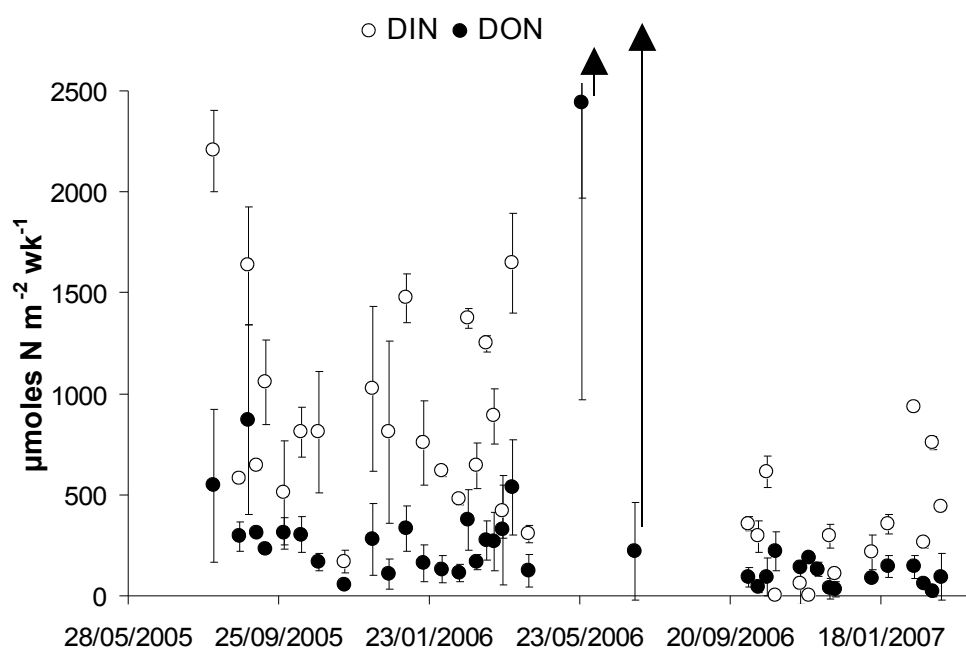


Figure 1: Weekly deposition of DIN and DON in $\mu\text{moles N m}^{-2}$ to standard bulk samplers. Error bar shows standard deviation of 3 replicate samplers.
DIN (25/05/2006, 2870 $\mu\text{moles N m}^{-2}$), DIN (6/07/2006, 4860 $\mu\text{moles N m}^{-2}$)

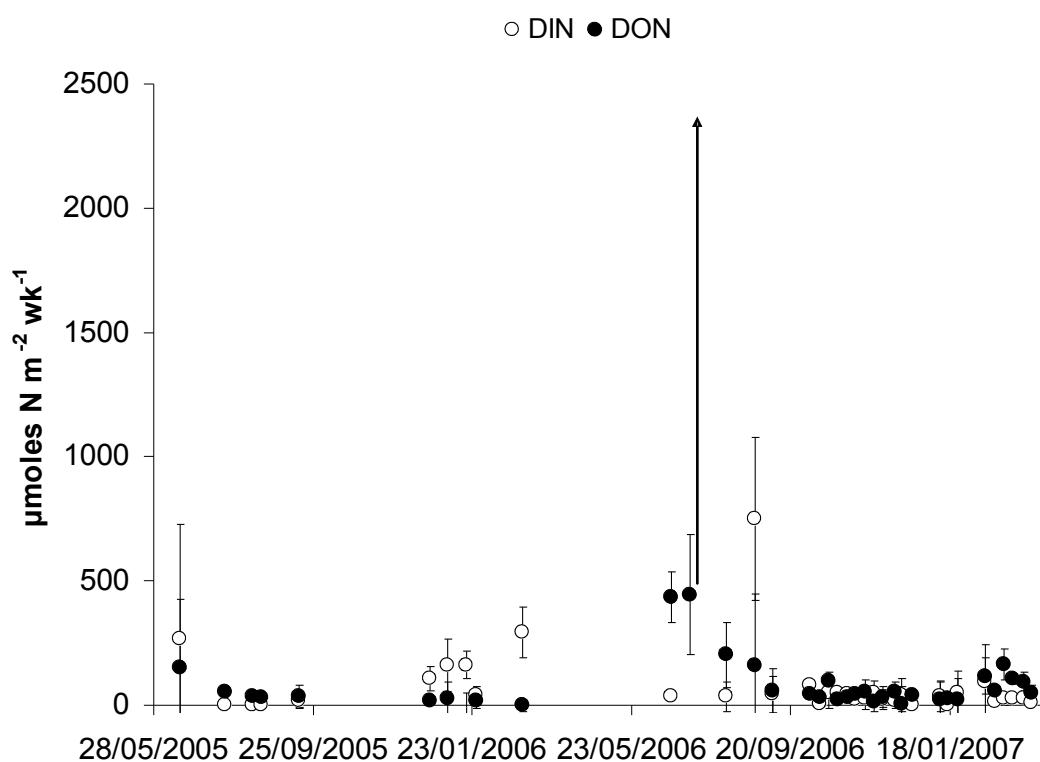


Figure 2: Weekly deposition of DIN and DON in $\mu\text{moles N m}^{-2}$ as wet deposition to flushing samplers. Error bar shows standard deviation of 3 replicate samplers.
DIN (6/07/2006, 3020 $\mu\text{moles N m}^{-2}$)

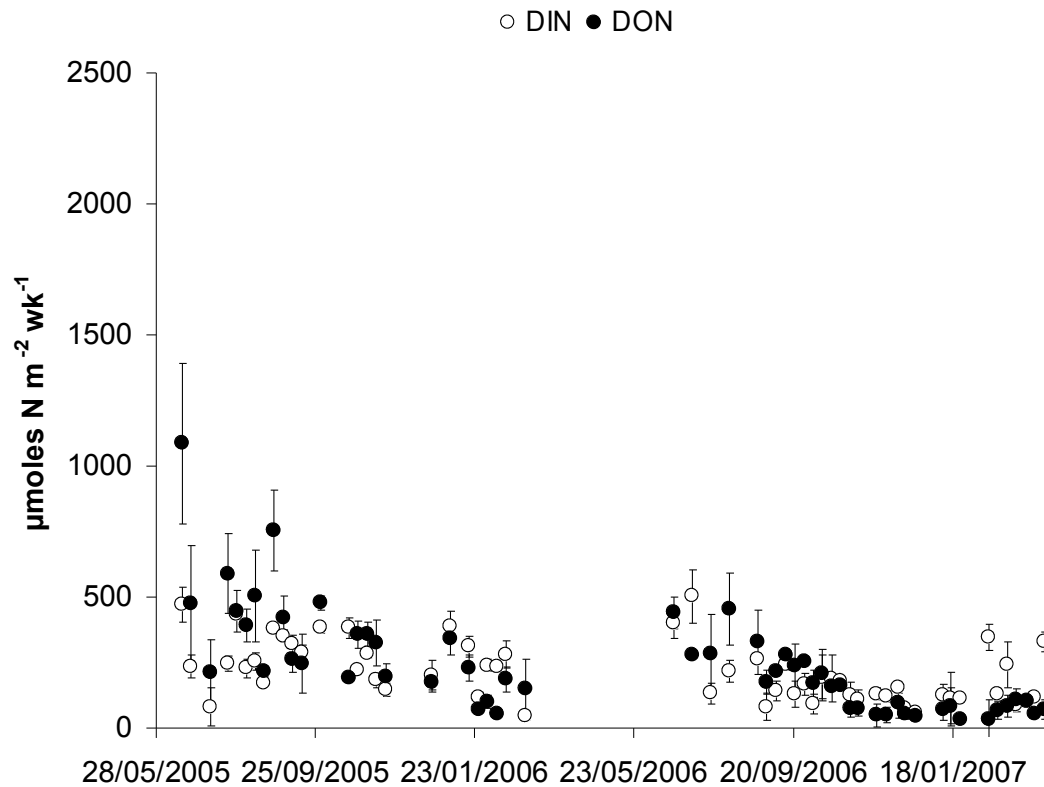


Figure 3: Weekly deposition of DIN and DON in $\mu\text{moles N m}^{-2}$ as dry deposition (funnel washings) to flushing samplers. Error bar shows standard deviation of 3 replicate samplers.

Figures 4, 5 and 6 represent the percentage of DON relative to TDN found in each type of collector: bulk deposition, wet deposition and funnel washings, respectively. Only weeks with three valid replicates for each type of collector were included in the analysis.

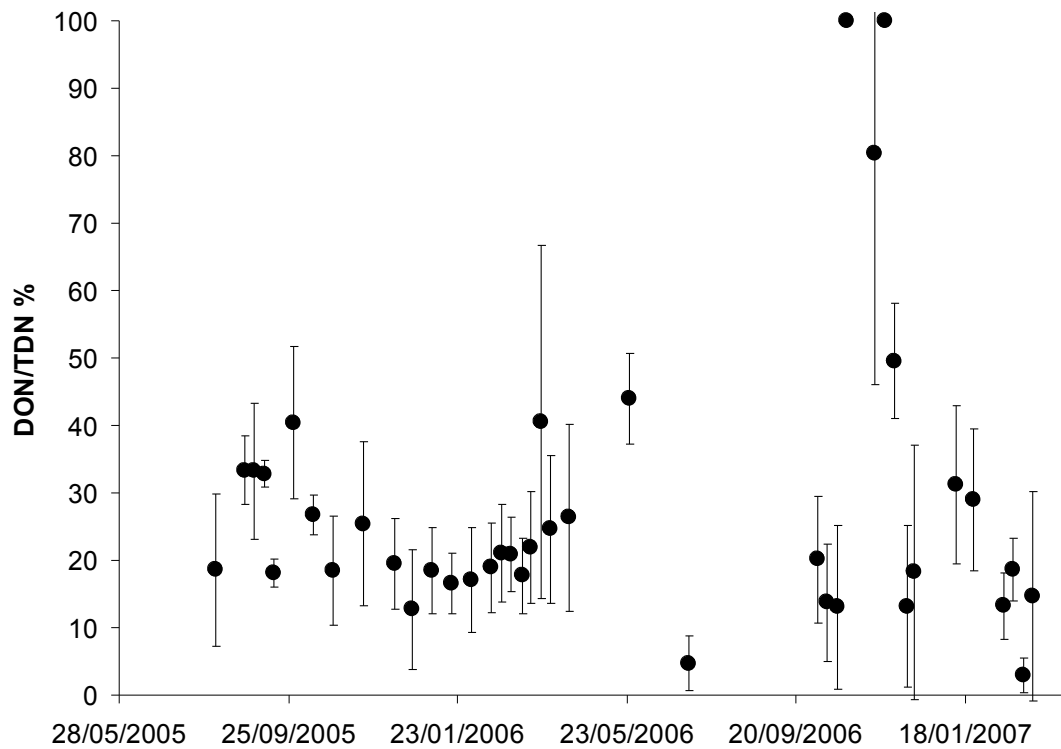


Figure 4: Weekly percentage of DON relative to TDN in bulk deposition.
Error bar shows standard deviation of 3 replicate samplers

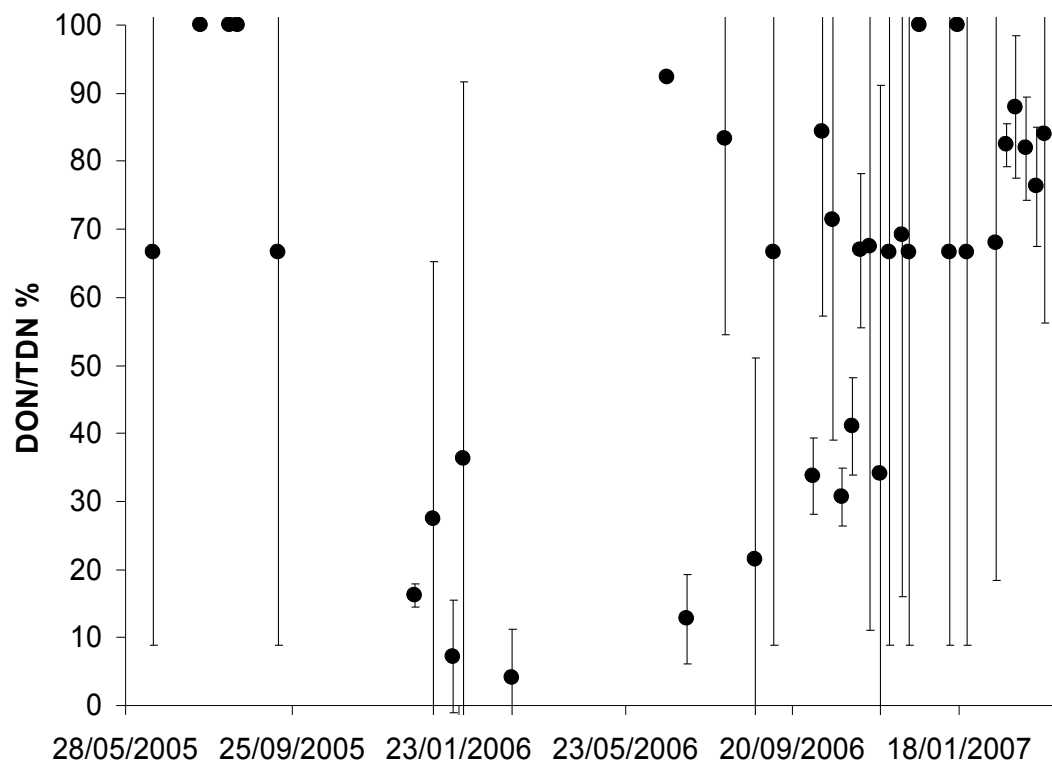


Figure 5: Weekly percentage of DON relative to TDN in wet deposition.
Error bar shows standard deviation of 3 replicate samplers.

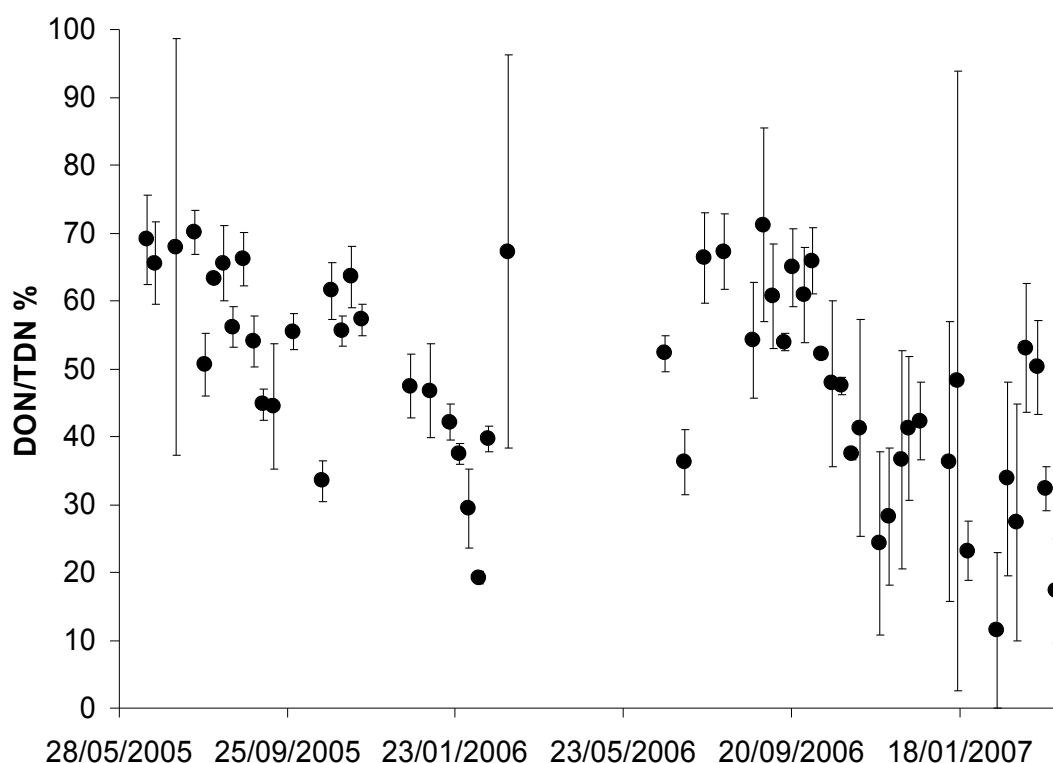


Figure 6: Weekly percentage of DON relative to TDN in dry deposition (funnel washings). Error bar shows standard deviation of 3 replicate samplers.

Note that some of the DON may have been formed from transformation of DIN during sampling rather than being present originally in wet deposition (see text). The data corresponding to the 25th of May 2006 and to the 6th of July 2006 have been included in the figures 1 to 6, but have not been included in the statistical analysis, as mineral nitrogen fertilizer was being applied to a nearby field on these dates, and may account for the large peaks in N deposition. However, 6th July 2006 is the only date in the whole period for which TDN in wet deposition was significantly higher than in dry deposition.

Table 1 presents the average amount of TDN and DON deposited in each type of collector, the average DON % relative to TDN, the average concentration of TDN and DON in rain, and the average volume of sample collected, either from rain (in bulk and wet deposition), or from washings (as dry deposition). The table is split into 2 parts: the first includes weeks with 3 valid replicates for at least one type of collector (38, 35 and 56 weekly samples for bulk, wet deposition and washings, respectively). The second part includes the 27 weekly samples with 3 valid replicates for all the 3 types of samples (bulk, wet deposition and washings). In this table, the standard deviation corresponding to the average amount deposited in the collector, the average sample volume, and the average concentration in rain is referred to the differences between independent collectors of the same type. The standard deviation for the DON % relative to TDN, on the other hand, is referred to the differences in the average deposition between the weeks included in that period. It has been presented in this way so the reader can have a grasp of the magnitude of deposition variability between weeks.

In theory, the addition of the washings and wet deposition together should be the same as bulk deposition. The large discrepancies found between bulk deposition and (wet + dry) deposition for N-containing solutes, but not other solutes (Cape et al., 2009), will be discussed in the section “Standard versus Flushing rain gauges”.

In a significant number of weeks, large differences were found between independent replicate samples, for both types of sampler, particularly for the wet deposition collectors. In most cases, the largest relative uncertainty in the DON: TDN ratio is caused by low concentrations of nitrogen species in the sample, and the combined uncertainties associated with each of the species involved in the calculation of DON. The low concentration of TDN in wet deposition, compared to bulk deposition, is discussed below.

Dry Deposition versus Wet Deposition

In most of the samples, the dry deposition fraction (funnel washings) of water soluble N-containing species (both organic and inorganic) is significantly larger than the wet deposition fraction. The weekly TDN deposition data (absolute amount, in $\mu\text{moles N m}^{-2} \text{ week}^{-1}$) from wet and dry deposition to the flushing gauge is represented in Figure 7. For comparison purposes, only the 49 weeks with 3 valid replicates for (dry + wet) deposition have been included (RSD <50% for sum of wet + dry deposition within replicates).

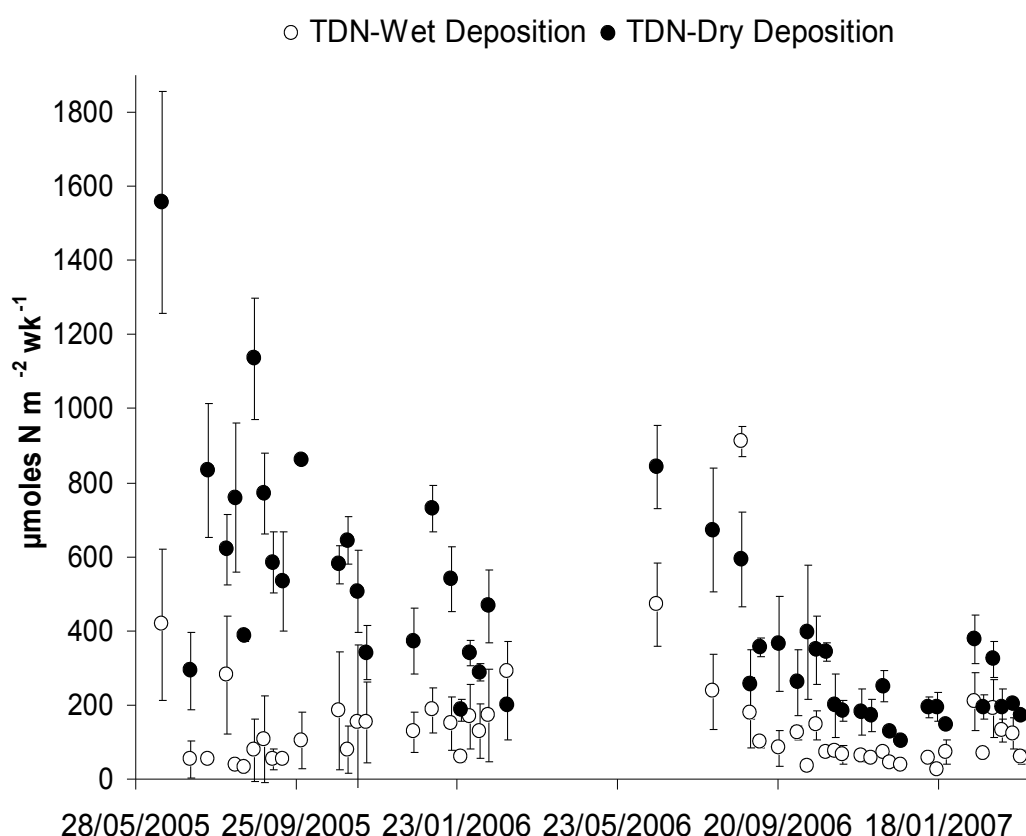


Figure 7: Weekly wet and dry deposition of TDN in $\mu\text{moles N m}^{-2}$ to the flushing samplers. Error bar shows standard deviation of 3 replicate samplers. Data for 6/7/2006 omitted because of likely contamination from local agricultural activity (cf. Figure 2).

Results from two-way ANOVA statistical analysis for this set of data, after a Box-Cox transformation (power 0.6) was applied to the data (which were approximately log-normally distributed) in order to fulfil the assumptions of the model, showed highly significant ($P < 0.001$) effects of sample date and sample type (wet or dry). The main source of variation corresponds to the variation between the two types of sample from the flushing rain gauges (dry and wet deposition). This effect is even larger than the one corresponding to sample date, which was expected to be very large. These results are in good agreement with the consistent differences between dry and wet deposition observed in figure 7. The interaction term in the ANOVA was also significant ($P < 0.001$), but in only one week, out of 49 weeks with 3 valid replicates, was the amount of TDN collected from wet deposition clearly larger than from dry deposition.

Standard versus Flushing rain gauges

Washing mechanism off: 15-week period (from 10/03/06 to 15/06/2006)

For a period of 15 weeks (from 10/03/06 to 15/06/2006) the flushing-washing mechanism of the flushing rain gauges was turned off, leaving the PTFE valve open to the rain collector. Data from this period allows direct comparison of bulk deposition between the standard rain gauges and the flushing rain gauges. For comparison purposes and statistical analysis, only 5 weeks out of the 15-week period had 3 valid replicates for both types of rain gauge. Bulk weekly TDN deposition ($\mu\text{moles N m}^{-2} \text{ wk}^{-1}$) in standard and (non-operating) flushing rain gauges is represented in Figure 8.

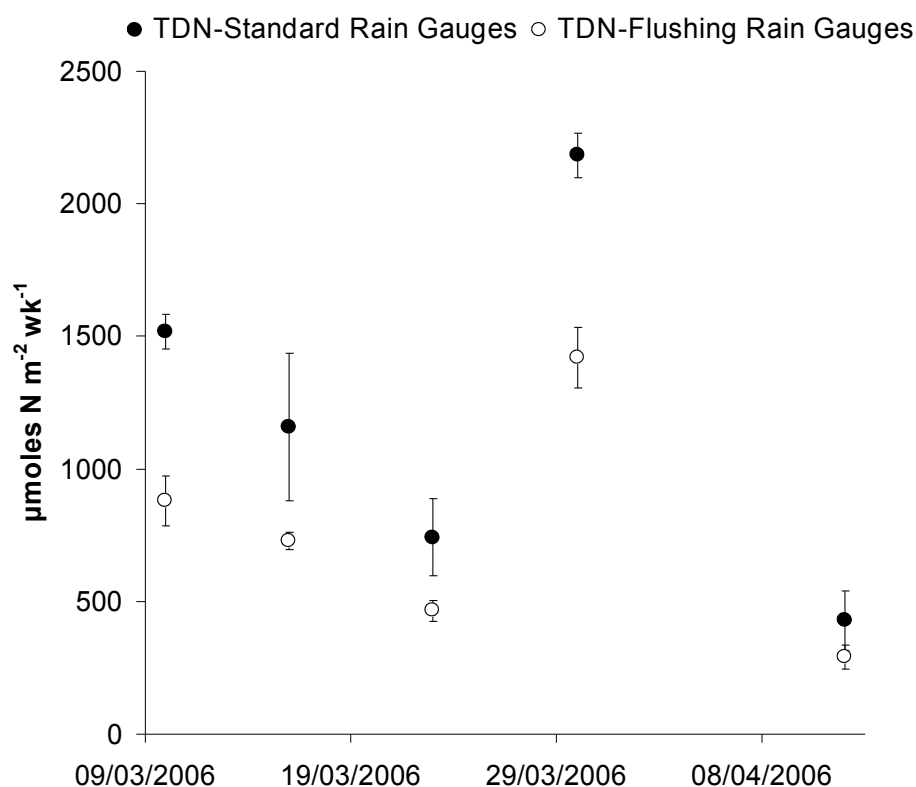


Figure 8: Weekly bulk deposition of TDN in $\mu\text{moles N m}^{-2}$ in standard and ‘non-operating’ flushing rain gauges. Error bar shows standard deviation of 3 replicate samplers.

Figure 8 clearly illustrates that the amount of TDN collected in all the 5 weeks with 3 valid replicates was larger in the standard rain gauges than in the flushing rain gauges, as confirmed by two-way ANOVA, with $P < 0.001$ for both main effects of date and gauge type. This was an unexpected outcome, as the prior expectation is that both types of rain gauge (standard and flushing) should behave exactly the same when the flushing-washing mechanism was not in operation.

Initially, evaporation losses in standard rain gauges were contemplated as a plausible explanation for the discrepancies between standard rain gauges and flushing rain gauges. Such losses would explain the larger overall concentration of N species in standard rain gauges, as well as the lower concentrations of organic nitrogen species (see below - “DON production in flushing rain gauges”), which might include an important fraction of volatile compounds that would be lost along with water in the case of evaporation. However, this hypothesis was disproved by the experimental evidence, as no significant differences were observed between the rainfall amount between standard and flushing rain collectors (differences $< 5\%$) or the concentrations of other solutes such as sodium, calcium, chloride and sulphate (Cape et al., 2009).

After discarding losses due to evaporation as an explanation, the most likely reason for the different behaviour of the two types of collector is losses of N-species along the 1.5 m long silicone tubing which connects the funnel to the rain collector in the flushing rain gauges, but not in the standard gauge, in which the funnel is connected directly to the sample bottle. Losses could either be due to biological activity in the tubing, which is a thymol-free area, despite being kept dark, or due to ion exchange processes between the sample and the silicone walls of the tubing. The extent of this effect is expected to be quite variable, as it would be strongly influenced by a number of factors such as temperature and rain volume. This loss of N during the sampling process has implications for estimating the relative importance of dry and wet deposition, as discussed below.

Washing mechanism on

Flushing rain gauges were performing as designed, i.e. discriminating between dry and wet deposition, for a period of 77 weeks. Figure 9 represents the total amount of TDN collected in standard rain gauges and in flushing rain gauges (washings + rain) each week. Only the 27 weeks with 3 valid replicates in each type of collector are included in the plot and in the statistical analysis.

In this period of “washings on”, there was also a tendency for a larger amount of N-containing species to be collected in standard rain gauges than in flushing rain gauges, but it is not so clear as in the period of “washings off”, with a number of weeks with larger TDN collection in the flushing rain gauges than in the standard ones. ANOVA analysis of the dataset (after log-transformation) is consistent with these findings: variation between dates is the main source of variation, but the difference between the two types of rain gauges is still significant ($P < 0.001$).

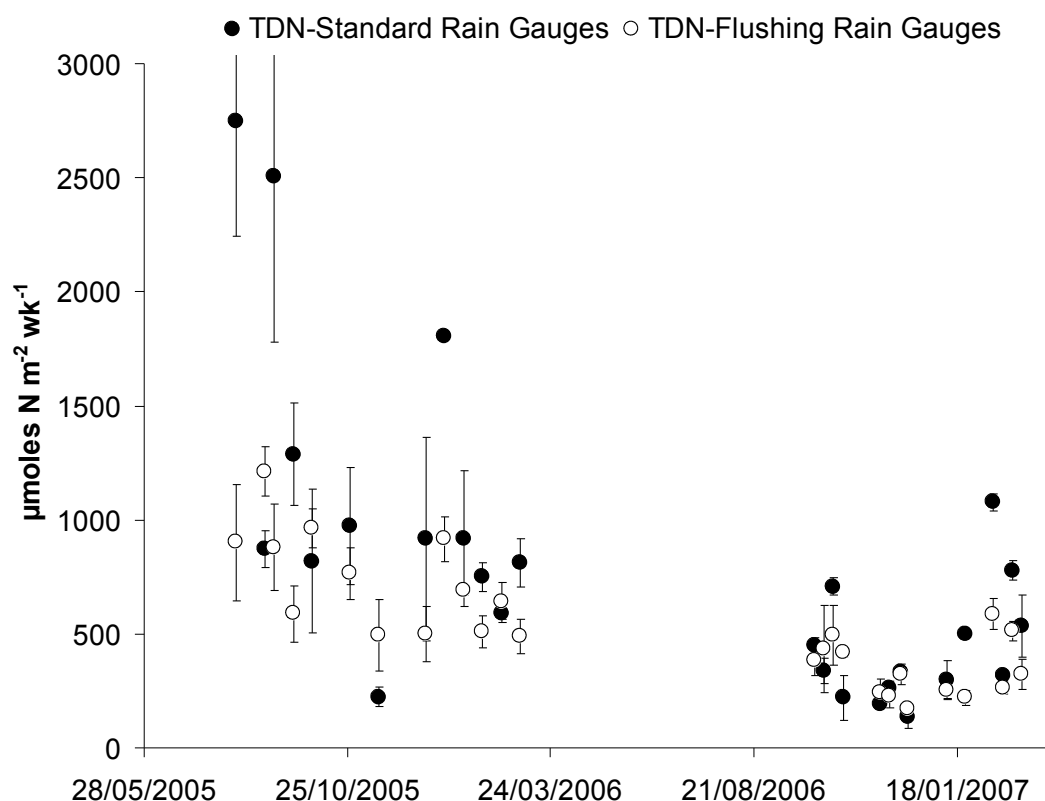


Figure 9: Weekly amount of TDN in $\mu\text{moles N m}^{-2}$ in standard rain gauges (bulk deposition) and flushing rain gauges (dry + wet deposition). Error bar shows standard deviation of 3 replicate samplers.

The same reasons as during the period with washings switched off would explain results for those weeks with larger TDN collection in standard rain gauges than in flushing rain gauges, i.e. N losses along the 1.5 m long silicone tubing, either due to biological activity (as this is a biocide-free area) or due to ion exchange processes along the silicone wall surface. The results for those weeks with larger TDN amounts collected in the flushing rain gauges than in standard rain gauges could arise from one or more of the following:

- i) a number of short and not very intense rain events during the collection period. (A short rain event would be enough to activate the washing mechanism in the flushing rain gauges, therefore efficiently collecting all dry deposition accumulated on the funnel surface. In the case of the standard rain gauges, on the other hand, the same short rain event might not have washed the funnel surface so efficiently and, therefore, the amount of N-species collected might be significantly smaller, at least the fraction coming from dry deposition).
- ii) release of material retained on the tubing surfaces during the preceding sampling period (tubing was not cleaned each week)
- iii) more efficient removal of dry-deposited material from the funnel surface by the 10% methanol wash solution than by rainfall.

DON “production” in flushing rain gauges

In the 27 weeks with 3 valid independent replicates for each type of rain gauge, the total amount of TDN collected in standard rain gauges was $22 \pm 3 \text{ mmoles N m}^{-2}$, and

in the flushing ones (rain + washings) was 15 ± 1 mmol N m⁻². However, the total amount of DON collected in the standard rain gauges was 5 ± 1 mmol N m⁻², and in the flushing ones (rain + washings) was 7.0 ± 0.4 mmol N m⁻². The type of gauge collecting smaller amounts of TDN (flushing rain gauge) collected larger amounts of DON (compare figure 9 with figure 10). The most likely explanation is that a portion of the ‘lost’ DIN is being transformed into DON inside the flushing rain gauges. Where and how this transformation occurs is a matter for further investigation.

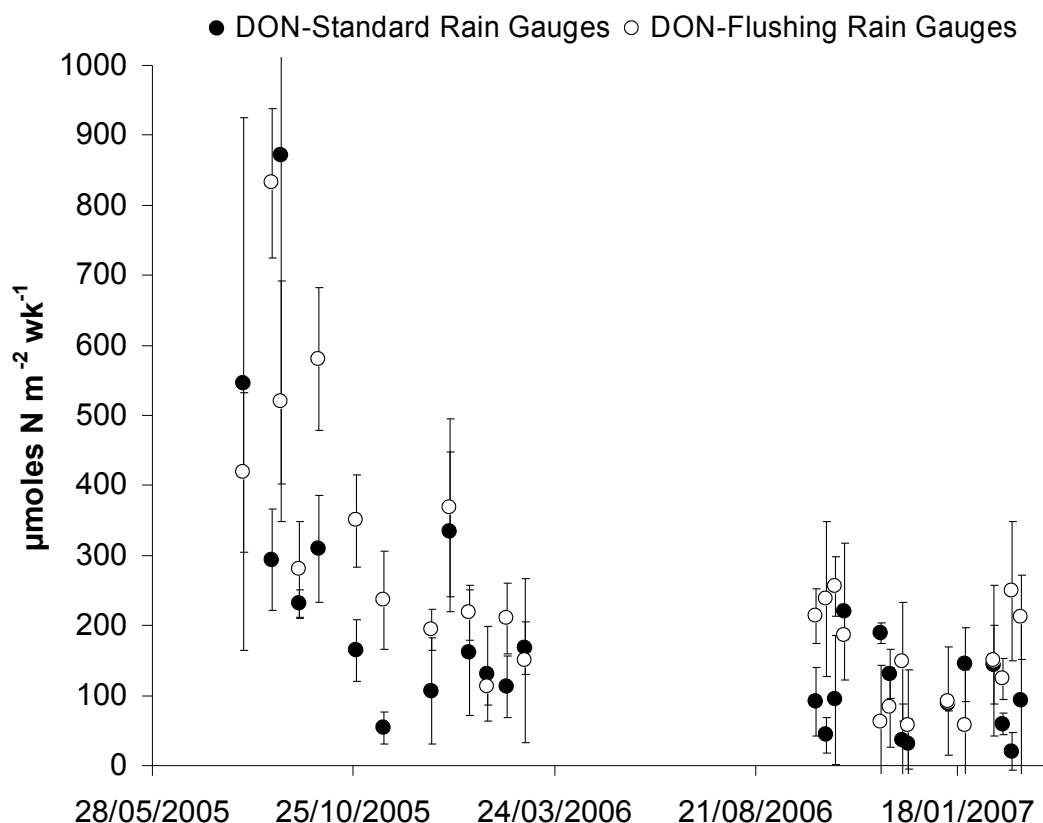


Figure 10: Weekly amount of DON in $\mu\text{mol N m}^{-2}$ in standard rain gauges (bulk deposition) and flushing rain gauges (dry + wet deposition). Error bar shows standard deviation of 3 replicate samplers.

Estimation of the relative contribution of wet and dry deposition

The lower and upper bounds to the contribution of dry deposition to the material collected by the standard rain gauge can be estimated from the above results as follows. If all transformations between different N forms are ignored (i.e. working with only the TDN data) then there are two extreme cases: (1) none of the dry deposited material was lost during sampling (a reasonable assumption as it was in 10% methanol solution), in which case the contribution of dry deposition to TDN is given by the amount collected as dry deposition as a fraction of the total collected by the standard gauge, i.e. over the 27 weeks of valid samples, $7.5/14.2 = 53\%$ (Table 1); or (2) if the losses of N in the flushing gauge were entirely caused by losses from the dry deposition sample, the fraction of dry deposition would rise to $(14.2-2.3)/14.2 = 84\%$.

For DIN, if transformations from DIN to DON are discounted and no losses from the washings occurred (case 1), the DIN deposited as dry deposition was $3.8/10.9 = 35\%$ of the DIN in the standard sampler (Table 1). For case 2 (losses of DIN were all from washings) the contribution of dry deposition of DIN increases to $(10.9-1.5)/10.9 = 86\%$. For DON, the average amount sampled as 'dry' deposition exceeded that recorded in the standard gauge (Table 1), implying either significant transformation from DIN to DON in the flushing sampler, or that all DON was dry-deposited.

Estimation of the relative contribution of DON to wet and dry deposition

The loss of N from the flushing sampler leads to uncertainties in the apparent fraction of TDN contributed by DON, especially with the evidence that some transformation of DIN to DON occurred. For the standard bulk sampler, DON represented $23 \pm 6\%$ of TDN over the 27 weekly samples for which there was a complete data set, or $24 \pm 7\%$ of TDN for the 38 weekly samples for which there were 3 replicate standard bulk samples (Table 1). These figures should be compared with a value of 26% for 7 weekly samples at the same site in 2000 (Cape et al., 2001) or 33% for 54 weekly samples in 2000-2 (Cape et al., 2004) using steel and glass bulk samplers, rather than polyethylene funnels and bottles. The construction materials may not be important, given that the earlier study showed no significant difference between different construction materials.

The present study suggests that the contribution of DON to TDN may differ between wet and dry deposition. For wet deposition, the proportion of DON in the collected samples was $36 \pm 9\%$, but the contribution of DON to wet deposition as measured in the standard bulk sampler is uncertain because of the losses in the flushing sampler. Because on average more DON was found in the combined (wet+dry) deposition than in the standard sampler, despite overall losses of TDN, this figure represents the upper bound to the contribution of DON to wet deposition. The fraction could have been as low as 12%, calculated as the amount of DON measured in wet deposition relative to TDN in the standard sampler less TDN measured as dry deposition, i.e. assuming all the 'missing' N from the flushing sampler was originally present as DIN. However, this figure might be even lower, as it has been calculated assuming that no transformation of DIN into DON occurred in wet deposition. By similar arguments, the measured contribution of DON to dry deposition can be calculated as $49 \pm 4\%$ based on analysis of the funnel washings, but this could include at least $16 \pm 15\%$ from conversion of DIN to DON in the washings, calculated from the excess of DON measured in the flushing samplers compared with the bulk samplers (Table 1). The contribution of DON to dry deposition of TDN is therefore likely to be 33% or less. The lower bound can be calculated assuming all the 'missing' N in the flushing sampler is DIN, and that the smallest contribution from DON in the dry sampler occurs if none of the DON in the wet sampler comes from conversion of DIN, giving a value of 21%.

Conclusions

1-This study presents further evidence of the importance of water soluble organic nitrogen (WSON) species in the boundary layer. On average, over the 27 weekly samples with 3 valid replicates for all the collectors, dissolved organic nitrogen

(DON) represented $23\pm 6\%$ of the total dissolved nitrogen (TDN) measured in bulk deposition, similar to the proportion of DON observed at this site previously.

2- The relative contribution of DON to TDN in wet and dry deposition is uncertain because of losses of N within the flushing sampler, but the upper bound to the contributions is $36\pm 9\%$ for wet deposition and $33\pm 15\%$ for dry deposition.

3- Dry deposition of particles and gas on the funnel surface, rather than deposition in rain, seems to be the main source of N-containing species (both inorganic and organic) to the bulk sampler, contributing between 53% and 84% of total N.

4- In general, larger amounts of N-containing species were collected in the standard bulk samplers than in the flushing samplers. This was particularly true during the period when the washings were not in operation (from 10/03/06 to 15/06/2006). This result implies chemical or biological interactions in the tubing leading from the funnel to the sampling bottle, which might be reduced by replacing silicone tubing with PTFE tubing, and by changing the tubing on each sampling occasion. This finding has implications for all types of precipitation sampler in which the funnel and the sample bottle are separated by a length of tubing – a common design.

5- In the flushing rain gauges, dissolved inorganic nitrogen (DIN) seems to be transformed into DON. This phenomenon requires further investigation. Biological activity transforming DIN into DON in the tubing would be a plausible explanation, despite the lack of light. It would be restricted only to the tubing, as both collecting bottles (rain and washings) are protected with thymol (a very effective biocide) against biological degradation. Another explanation might be in the rinsing solution for the washings, which contains 10% methanol to aid wetting of the funnel surface and to prevent freezing of the wash solution. Chemical reaction between DIN and methanol to produce organic material is unlikely, but the methanol wash solution may be more effective at removing dry deposited organic nitrogen from the funnel than rain water.

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Table 1. Amounts and concentrations of water-soluble nitrogen (total and organic) and rainfall amount deposited to each type of precipitation sampler (bulk, flushing) throughout the study period, for weeks in which there were valid samples from each of the 3 replicate samplers of each type.

	Average Amount Deposited/ $\mu\text{mol N sample}^{-1}$		Standard Deviation of Amount Deposited in 3 replicate samplers/ $\mu\text{mol N sample}^{-1}$		Average % DON relative to TDN over all samples	Standard Deviation of %DON across all weekly samples	Average Rain Volume Collected/ L sample ⁻¹		Average Concentration in rain sample/ μM		Standard Deviation of Concentration across 3 replicate samplers/ μM		
	TDN	DON	TDN	DON	DON	DON	Avg	St. Dev.	TDN	DON	TDN	DON	
Bulk Dep.	15.9	3.8	1.8	1.1	24	21	0.41	0.005	61.0	14.0	4.7	3.5	38 weeks with 3 valid replicates
Wet Dep.	2.6	1.2	0.2	0.3	47	33	0.36	0.005	9.9	5.4	0.8	0.3	35 weeks with 3 valid replicates
Washings (Dry Dep.)	8.1	4.3	0.4	0.2	53	16	0.30	0.009	N/A	N/A	N/A	N/A	56 weeks with 3 valid replicates
Bulk Dep.	14.2	3.3	1.7	0.9	23	23	0.39	0.008	56.1	11.5	3.6	2.4	27 weeks with 3 valid replicates for bulk and (wet+dry) deposition
Wet Dep.	2.3	0.8	0.2	0.2	36	35	0.36	0.012	10.8	3.7	1.8	0.3	
Washings (Dry Dep.)	7.5	3.7	0.4	0.2	49	15	0.35	0.013	N/A	N/A	N/A	N/A	
Wet+Dry Dep.	9.8	4.5	0.7	0.2	46	13	N/A	N/A	N/A	N/A	N/A	N/A	